Photoisomerization Ability of Molecular Switches Adsorbed on Au(111):
Comparison between Azobenzene and Stilbene Derivatives

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Table of Contents

Synthesis S2
Spectroscopy and Switching in Solution S4
Synthesis

**General Methods.** Solvents and starting materials were used as received. THF was distilled under an argon atmosphere over sodium prior to use. All reactions were performed in an argon atmosphere. Column chromatography was carried out with 130 - 400 mesh silica gel. NMR spectra were recorded on a 400 MHz (100.6 MHz for $^{13}$C) Bruker AV 400 or on a 300 MHz (75.6 MHz for $^{13}$C) Bruker DPX 300 spectrometer at 27 °C using residual protonated solvent signals as internal standard ($^1$H-NMR: $\delta$(CDCl$_3$) = 7.24 ppm, $\delta$(CD$_3$CN) = 1.94 ppm, and$^{13}$C-NMR: $\delta$(CDCl$_3$) = 77.0 ppm, $\delta$(CD$_3$CN) = 1.32 ppm). Mass spectrometry was performed on Thermo LTQ FT instrument (ESI, ESI-HRMS: additives of mixtures of MeOH/H$_2$O75/25 + 0.5% formic acid) and MSI concept 1H (EI, 70eV ionization) as well as on a QSTARXL Applied Q-TOF with a ISV of 950 V. HPLC separations were performed with Shimadzu LC-10A systems equipped with a photodiode array detector (PAD or DAD) or with Waters Alliance systems (mixtures and gradient mixtures of acetonitrile/water) equipped with150 x 2 mm Luna columns (3 μm, phenyl-hexyl material). The Waters systems consisted of a Waters Separations Module 2695, a Waters Diode Array detector 996 and a Waters Mass Detector ZQ 2000.

*Trans-3,3’,5,5’-tetra-tert-butyl-azobenzene* (trans-TBA) was synthesized as described by us previously.$^1$ *Trans-3,3’,5,5’-tetra-tert-butylstilbene* (trans-TBS) was synthesized by the following route (Figure S1):

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Figure S1. Synthesis of \textit{trans}-3,3',5,5'-tetra-\textit{tert}-butylstilbene (\textit{trans-TBS}).

\textit{Trans-3,3',5,5'-tetra-\textit{tert}-butylstilbene (\textit{trans-TBS}).} \textsuperscript{2} Di-\textit{tert}-butylbromobenzene 1 (167 mg, 0.6 mmol), catecholborane 4 (200 mg, 0.6 mmol), 11 mL of toluene, 5.5 mL of 1 M aqueous NaOH-solution, and 20 mg (0.04 mmol) of Pd(Ph\textsubscript{3})\textsubscript{4} were mixed in a dried Schlenck flask and degassed 3 times. The mixture was heated at 110 °C for 17 h. After cooling to room temperature the layers were separated and the aqueous phase was washed with toluene. The organic phase was washed with brine and dried with MgSO\textsubscript{4}. After column chromatography (silica gel, neat PE), 82 mg of the product were obtained as colorless solid (34 \% yield). \(R_f\) (PE) = 0.24. \textsuperscript{1}H-NMR (CDCl\textsubscript{3}): \(\delta\) (ppm): 7.39 (d, 4H, \textsuperscript{3}J = 1.8 Hz, Ar-H), 7.34 (t, 2H, \textsuperscript{3}J = 1.8 Hz, Ar-H), 7.13 (s, 2H, C-H), 1.37 (s, 36 H, \textit{t-Bu}). \textsuperscript{13}C-NMR (CDCl\textsubscript{3}): \(\delta\) (ppm) = 150.9, 136.7, 129.0, 121.8, 120.8, 34.8, 31.5. MS (EI, 70-85 °C) m/z = 404 [M]+, 57. HPLC (CH\textsubscript{3}CN+ (grad 0-30\%) water) \(t_{ret}\) = 17.4 min (94\% peak area).

Spectroscopy and Switching in Solution

UV-visible absorption spectra were recorded, using quartz cuvettes of 1 cm length on a Cary 50 spectrophotometer equipped with a Peltier-thermostated cell holder at 25 ± 0.05 °C. All solvents employed in optical spectroscopy studies were of spectrophotometric grade. Analytical irradiation experiments were performed on degassed solutions (Ar for 5 min, 2 - 4·10⁻⁵ M) using a LOT-Oriel 1000 W medium-pressure xenon lamp (XBO). For photochemical trans → cis isomerization (Figure S2, right), two cut-off filters providing λₘₐₓₜ = 336 nm (hwfm = 47 nm, T = 33%) were used, while for photochemical cis → trans isomerization a narrow interference filter λₘₐₓₖ = 254 nm (T = 33%) was used. Quantitative UV/vis spectra of the cis-TBS were determined combining spectroscopy and chromatography data (Figure S2, left) and no thermal cis → trans isomerization was observed.

![Figure S2](image_url)

**Figure S2.** Top: UV/vis absorption spectra of trans-TBS (λₘₐₓₜ = 302 nm, ε = 21300) and cis-TBS (λₘₐₓₖ = 265 nm, ε = 8100) in cyclohexane solution at 25 °C. Bottom: Photochemical trans → cis isomerization (λᵢᵣᵣ = 336 nm), yielding 94% cis-TBS in the photostationary state.